

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference GB2 2002087 PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)
International application No. PCT/EP 03/09314	International filing date (day/month/year) 30.07.2003	Priority date (day/month/year) 30.07.2002
International Patent Classification (IPC) or both national classification and IPC C23C16/40		
Applicant SAINT-GOBAIN GLASS FRANCE et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 9 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains Indications relating to the following items:
 - I Basis of the opinion
 - II Priority
 - III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV Lack of unity of invention
 - V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI Certain documents cited
 - VII Certain defects in the international application
 - VIII Certain observations on the international application

Date of submission of the demand 01.10.2003	Date of completion of this report 29.10.2004
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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP 03/09314

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-10 as originally filed

Claims, Numbers

1-23 received on 06.09.2004 with letter of 06.09.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2,3,10,21
	No:	Claims	1, 4 - 9, 11 - 23
Inventive step (IS)	Yes:	Claims	
	No:	Claims	2,3,10
Industrial applicability (IA)	Yes:	Claims	1 - 23
	No:	Claims	

2. Citations and explanations

see separate sheet

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EXAMINATION REPORT - SEPARATE SHEET**

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Re Item I

Basis of the report

Claims 22 and 23, which were submitted with letter of September 6, 2004, are considered to go beyond the original disclosure and, hence, do not meet the provisions of Article 34(2)(b) PCT.

a) Claim 22: A film being "crystallized" is considered to be predominantly in a crystalline state, whereas a film having a "degree of crystallinity" may be fully crystallized but may also comprise only some micrometer-sized nuclei. A degree of crystallinity which corresponds to a substantially complete crystallization is not described in the original disclosure.

In addition, this claim being directed to a substrate cannot depend on method claim 21.

b) Claim 23: Although the feature that the absorption levels are in a range from a few percent to less than one can be found in Example 2, there is no combination of this feature in the example with the other features of this claim.

Therefore, the examination is based on the originally filed claims 23 and 24.

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

- D1: PATENT ABSTRACTS OF JAPAN vol. 2000, no. 14, 5 March 2001 (2001-03-05) & JP 2000 313962 A (SEKISUI CHEM CO LTD), 14 November 2000 (2000-11-14)
- D2: PATENT ABSTRACTS OF JAPAN vol. 1997, no. 02, 28 February 1997 (1997-02-28) & JP 08 253322 A (RES DEV CORP OF JAPAN), 1 October 1996 (1996-10-01)
- D3: US 2003/072891 A1 (FUKUDA KAZUHIRO ET AL) 17 April 2003 (2003-04-17)
- D4: WO 02 48428 A (KONISHIROKU PHOTO IND ;FUKUDA KAZUHIRO (JP); KONDO YOSHIKAZU (JP);) 20 June 2002 (2002-06-20)
- D5: US-A-5 993 916 (LUO LEE ET AL) 30 November 1999 (1999-11-30)
- D6: US 2001/025205 A1 (LIAO MARVIN ET AL) 27 September 2001 (2001-09-27)

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D7: US-B1-6 329 237 (KIM KYONG MIN ET AL) 11 December 2001 (2001-12-11)

D8: US 2002/086476 A1 (KIM KYONG-MIN ET AL) 4 July 2002 (2002-07-04)

D9: US-A-5 295 220 (HEMING MARTIN ET AL) 15 March 1994 (1994-03-15)

2.

2.1. Technical problem stated by the Applicant.

To provide a CVD process for TiO₂, which allows for high throughput and low substrate temperatures at low costs.

2.2. Solution proposed by the Applicant.

A process according to claim 1 is suggested, which uses an atmospheric pressure glow discharge plasma for the deposition of TiO₂ at substrate temperatures below 250°C. Use of a plasma allows these low substrate temperatures. High throughputs and low costs are achieved by avoiding a complex vacuum system into which and from which the substrates have to be transferred.

3. Prior art, novelty and inventive step (Article 33(2 and 3) PCT).

3.1. The idea to deposit TiO₂ films by a plasma CVD process at atmospheric pressure is not novel. For example D1 discloses such a process using a plasma based on a gas mixture of 0.005 - 5 vol % titanium tetraisopropoxide, 3 vol. % or less O₂, 60 - 97 vol. % Ar and 3 - 40 vol. % N₂. The plasma is an AC plasma having a frequency of 15 - 50 kHz. The substrate is placed between two electrodes. The process is suitable for polymeric substrates with lower melting points, which implies substrate temperatures below 250°C. TiO₂ films are commonly known to be photoactive due to their band gap (see also page 1, lines 2 - 4, of the present application). Every film modifies its surface energy to some extent upon irradiation with UV or visible light. The films produced in D1 are considered to have "some degree of crystallinity", also, because the process is similar to the one of the present application. There are no obstacles seen why the method of D1 should not be used together with further coating methods.

Hence, claims 1, 8, 11, 12, 17, 18, 22 and 23 lack novelty over D1.

The Japanese patent application and its computer-translation, provided by the JPO, reveal further details.

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First, Fig. 8 shows the apparatus employed for the atmospheric pressure CVD process. The apparatus comprises a showerhead 84, which apparently introduces a laminar flow of precursor gases, and an exhaust 811, which is considered as an extraction system. Usually, in CVD reactors using showerheads the laminar flow is maintained in the deposition zone. Such a system is considered to provide uniformities as in claim 9. [0025] - [0027] refer to the providing and maintaining of the glow discharge. In [0036] it is mentioned to use metals such as Cu, Al, brass, stainless steel or an intermetallic compound as electrode material. In [0035] it is mentioned to add some moisture to the gas mixture to promote decomposition of the titanium alkoxide precursor. It is, however, important to avoid that the moisture concentration is too high. The upper desirable limit is 500 ppm, which corresponds to 0.05 %. Film growth is 750 nm in 30 s, which is 25 nm/s ([0082] and [0083]). The method of D1 is considered to be suitable for coating a continuous film or a series of substrates supplied semi-continuously.

Hence, also claims 4, 5, 9, 13, 14, 16, 19 and 20 lack novelty with respect to D1.

Further it is assumed that the plasma density in D1 is below the values given in claim 15, because the process of D1 is quite similar than the one of the present application (see also the examples of the application). Therefore, also claim 15 lacks novelty. However, even if this claim would be novel it would not be considered inventive, because the determination of the plasma density is considered as an optimization of the known process of D1.

Claim 10 is not considered inventive, since it is obvious that thicker layers or layers of a different composition can be made by sequential coating.

Subject-matter of claims 6, 7 and 21 forms state of the art for CVD apparatuses. The skilled person would therefore consider also to equip the apparatus of D1 with such features.

3.2. Also D2 teaches an atmospheric glow discharge plasma CVD process using a titanium alkoxide for deposition of a TiO₂ layer. The Japanese patent application and its computer-translation, provided by the JPO, reveal further details. The substrate temperature may raise up to 200°C [0026]. The apparatus is suitable for providing a laminar precursor gas flow. Such an apparatus is considered to provide the uniformities given in claim 9. An extraction system is implied. Cooling is apparently provided to avoid overheating of the substrate [0026].

Note also that [0011] and [0030] mention use of He gas, as it is the case in the examples of the present application. [0040] describes a photolytic effect.

Claims 1, 4 - 9, 11, 17, 18, 20, 22 - 24 lack novelty with respect to D2.

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3.3. D3 has a publication date between the priority date and the filing date of the present application. It will not be discussed with respect to novelty and inventive step, because for the time being the priority date of the present application is assumed to be validly claimed. D3 discloses deposition of layers by atmospheric plasma CVD (abstract). The coating apparatus is shown in Fig. 1, including a gas extraction system. In the examples, TiO_2 is deposited on cellulose ester films. Hence, it must be assumed that the substrate temperature lies below 250°C. [0018] states that the electrodes are made of stainless steel and may adjust the temperature by water circulation. The plasma density is 0.03 W/cm². Ti precursors are mentioned in [0132].

3.4. D4 is only available in Japanese. However, EP1342810 is a family document, which claims the same priority dates and which is available in English. According to EP1342810 D4 relates to a method of producing anti-reflexion coatings onto organic films by plasma CVD at atmospheric pressure. Deposition of TiO_2 is described on pages 24 - 25. The apparatus and the coating method are taught on pages 6 - 13. Claims 1, 4 - 9, 11- 20 and 22 - 24 lack novelty over D4. Claims 10 and 21 are only considered as technical variations of D4.

3.5. With respect to the prior art documents D1 - D4 claims 2 and 3 are not derivable. However, post-treatment of ceramic films deposited by CVD is known in the art. D5 and D6 mention a plasma treatment of deposited TiN films to improve its electrical properties. It is common knowledge that the electrical properties are strongly related to the stoichiometry and crystallinity of the TiN films. D7 and D8 teach plasma treatment of Ta_2O_5 and of $(Ba, Sr)TiO_3$ films, the latter containing already TiO_2 , to improve their electrical properties by improvement of the crystallinity.

Therefore, subject-matter of claims 2 and 3 appears obvious to the skilled person. For example, if the skilled person is not fully satisfied with the optical and/or electrical properties of the TiO_2 films deposited by a method chosen from D1 - D4, he/she would consider the teaching of these documents, i.e. that plasma post-treatment of related TiN, Ta_2O_5 or $(Ba, Sr)TiO_3$ films may improve the electrical properties.

3.6. D9 is mentioned, because it teaches pre-treatment of a substrate before deposition of TiO_2 by a plasma CVD process (col. 3, line 5 - 9). Pre-treatment is also mentioned in the description of the present application.

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4. Industrial applicability (Article 33(4) PCT).

Claims 1 - 24 fulfill the requirement of industrial applicability, since subject-matter of present application can be made or used (in a technological sense) in industry (Article 33(4) PCT).

Re Item VI

Certain documents cited

Certain published documents

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
D3 = US2003/0072891	April 17, 2003	April 12, 2002	April 25, 2001

Re Item VII

Certain defects in the international application

The application does not comply with the provisions of Rule 5.1.a.ii PCT, because the most relevant prior art, such as documents D1 - D4 are not cited.

Re Item VIII

Certain observations on the international application

Clarity

1. It is not clear what exactly is meant in line 7 of claim 1.
2. Claims 9, 16 - 18, 20 and 22 - 24 are defined by the result to be achieved instead of by definition of technical features which, in combination with the known combination of technical features, would provide these results. A definition of claimed subject-matter by the result to be achieved is only allowable in exceptional cases (see PCT Gazette, section

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IV, paragraph III-4.7).

3. The expression that "the film has a degree of crystallinity" in claim 23 is relative, because it is unclear, what "degree of crystallinity" means: do nuclei comprising a few atoms but having regular interatomic distances already fall under this expression or are small crystals meant? In addition, depending on the structure determination procedure, such as XRD, TEM, and on the size of the "nuclei or crystallites", some materials will not appear crystalline if examined by one method but appear crystalline when examined by the other method.

4. The expression "good optical quality" in claim 24 is relative, because "good" has a different meaning for different persons.

5. Depending claim 3 refers to "the glow discharge post treatment". However in the preceding claims a glow discharge post treatment is not mentioned.

6. Depending claim 10 refers to "the direction of movement". However in the preceding claims a direction of movement is not mentioned.

7. Depending claim 13 refers to "the metal electrodes". However in the preceding claims metal electrodes are not mentioned.

Claims

1. Method for depositing titania, or titania-containing as thin films on a substrate, the method comprising the steps of:
 - using an atmospheric pressure glow discharge plasma as a major source of reaction to improve film properties and film growth rates, when the substrate is heated at a temperature below 250°C,
 - introducing a reactive titania CVD precursor which has been pre-vaporised into the introduced gas flow into a gas flowing through a coating region.
2. Method according to claim 1 wherein a post treatment of the coating with an atmospheric glow discharge plasma modifies the film properties and structure.
3. Method according to claim 2 wherein the glow discharge post treatment modifies the film stoichiometry allowing control of film properties.
4. Method according to claim 1 wherein a laminar flow is introduced into, and through the coating zone.
5. Method according to anyone of the claims 1 to 4 wherein an extraction system is employed to control gas flow through the coating zone which supports controlled flow.
6. Method according to anyone of the preceding claims wherein a thermal control system is designed into the coating zone to maintain the substrate temperature at the desired level, said thermal control system can be achieved by a range of techniques including gas or water or liquid coolant based cooling, or combinations thereof.
7. Method according to claim 6 wherein the thermal control system is designed to cool the coating zone to reduce unwanted side reactions.
8. Method according to claim 1 wherein the reactive titania CVD precursor which is introduced in the coating zone is an alkoxide of titanium or titanium tetrachloride.
9. Method according to anyone of the preceding claims wherein films can be deposited with a uniformity of at least +/- 20 % and preferably a uniformity of at least +/- 10 % and more preferably better than +/- 5%.

REPLACED BY
ART 34 AMDT

10. Method according to anyone of the preceding claims wherein it can be used to build up a thicker layer or layers of different composition by arranging sequential coating regions along the direction of movement of the substrate.
11. Method according to anyone of the preceding claims wherein it can be used in combination with different coating method.
12. Method according to claim 1 wherein the glow discharge plasma is generated, between electrodes, by a low frequency e.g. AF or RF source where the frequency is below 100KHz and preferably below 30Khz
13. Method according to claim 12 wherein the metal electrodes are selected from a material which reduces heat generation
14. Method according to claims 12 or 13 wherein the electrodes are made of brass.
15. Method according to anyone of the preceding claims wherein the power density of the plasma is below 5 Wcm^{-2} and preferably below 1Wcm^{-2} and more preferably below 0.5 Wcm^{-2} .
16. Method according to anyone of preceding claims, wherein the peak growth rate is at least 10 nm per second, and up to several tens of nm per second, over 100nm per second.
17. Method according to anyone of preceding claims, wherein the film can be deposited on preformed and/or thermally toughened substrates
18. Method according to anyone of preceding claim, wherein the film can be deposited on a wide range of temperature sensitive substrates including thermally preformed substrates and plastic substrate materials.
19. Method according to anyone of preceding claims, wherein a level of water and oxygen are controlled carefully to achieve target growth rates and to control unwanted side reactions, the oxygen level being below 5% and more preferably below 1%, the water vapour levels being controlled preferably below 1% and more preferably below 0.1%
20. Method according to claim 19, wherein it is suitable for coating moving substrates – both as continuous film or sheet, or a series of substrates supplied semi-continuously.
21. Method according to anyone of preceding claims, wherein one or more gas flushing zones is used to allow the introduction, and removal, of the substrates whilst maintaining the integrity of the coating region gas composition.

REPLACED BY
ART 34 AMDT

22. Substrate obtained by a method according to anyone of preceding claims, wherein the film is photo-active, demonstrated by their ability to destroy organic materials on the surface and/or to modify the surface energy on irradiation with UV or visible light.
23. Substrate according to claim 22, wherein the film has a degree of crystallinity
24. Substrate according to claim 22 or 23, wherein the deposited film has a good optical quality suitable, for example, for use on substrates which are required to be substantially transparent to the human eye and to be looked through.

REPLACED BY
ART 34 AMDT

PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

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International application No. PCT/EP 03/09314	International filing date (day/month/year) 30.07.2003	Priority date (day/month/year) 30.07.2002
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2. This REPORT consists of a total of 9 sheets, including this cover sheet.

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3. This report contains indications relating to the following items:

- I Basis of the opinion
- II Priority
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- IV Lack of unity of invention
- V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 01.10.2003	Date of completion of this report 29.10.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Hintermaier, F Telephone No. +49 89 2399-7063

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP 03/09314

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-10 as originally filed

Claims, Numbers

1-23 received on 06.09.2004 with letter of 06.09.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
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3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

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4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
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6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims	2,3,10,21
	No:	Claims	1, 4 - 9, 11 - 23
Inventive step (IS)	Yes:	Claims	
	No:	Claims	2,3,10
Industrial applicability (IA)	Yes:	Claims	1 - 23
	No:	Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
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Re Item I

Basis of the report

Claims 22 and 23, which were submitted with letter of September 6, 2004, are considered to go beyond the original disclosure and, hence, do not meet the provisions of Article 34(2)(b) PCT.

a) Claim 22: A film being "crystallized" is considered to be predominantly in a crystalline state, whereas a film having a "degree of crystallinity" may be fully crystallized but may also comprise only some micrometer-sized nuclei. A degree of crystallinity which corresponds to a substantially complete crystallization is not described in the original disclosure.

In addition, this claim being directed to a substrate cannot depend on method claim 21.

b) Claim 23: Although the feature that the absorption levels are in a range from a few percent to less than one can be found in Example 2, there is no combination of this feature in the example with the other features of this claim.

Therefore, the examination is based on the originally filed claims 23 and 24.

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

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2.

2.1. Technical problem stated by the Applicant.

To provide a CVD process for TiO₂, which allows for high throughput and low substrate temperatures at low costs.

2.2. Solution proposed by the Applicant.

A process according to claim 1 is suggested, which uses an atmospheric pressure glow discharge plasma for the deposition of TiO₂ at substrate temperatures below 250°C. Use of a plasma allows these low substrate temperatures. High throughputs and low costs are achieved by avoiding a complex vacuum system into which and from which the substrates have to be transferred.

3. Prior art, novelty and inventive step (Article 33(2 and 3) PCT).

3.1. The idea to deposit TiO₂ films by a plasma CVD process at atmospheric pressure is not novel. For example D1 discloses such a process using a plasma based on a gas mixture of 0.005 - 5 vol % titanium tetraisopropoxide, 3 vol. % or less O₂, 60 - 97 vol. % Ar and 3 - 40 vol. % N₂. The plasma is an AC plasma having a frequency of 15 - 50 kHz. The substrate is placed between two electrodes. The process is suitable for polymeric substrates with lower melting points, which implies substrate temperatures below 250°C. TiO₂ films are commonly known to be photoactive due to their band gap (see also page 1, lines 2 - 4, of the present application). Every film modifies its surface energy to some extent upon irradiation with UV or visible light. The films produced in D1 are considered to have "some degree of crystallinity", also, because the process is similar to the one of the present application. There are no obstacles seen why the method of D1 should not be used together with further coating methods.

Hence, claims 1, 8, 11, 12, 17, 18, 22 and 23 lack novelty over D1.

The Japanese patent application and its computer-translation, provided by the JPO, reveal further details.

First, Fig. 8 shows the apparatus employed for the atmospheric pressure CVD process. The apparatus comprises a showerhead 84, which apparently introduces a laminar flow of precursor gases, and an exhaust 811, which is considered as an extraction system. Usually, in CVD reactors using showerheads the laminar flow is maintained in the deposition zone. Such a system is considered to provide uniformities as in claim 9. [0025] - [0027] refer to the providing and maintaining of the glow discharge. In [0036] it is mentioned to use metals such as Cu, Al, brass, stainless steel or an intermetallic compound as electrode material. In [0035] it is mentioned to add some moisture to the gas mixture to promote decomposition of the titanium alkoxide precursor. It is, however, important to avoid that the moisture concentration is too high. The upper desirable limit is 500 ppm, which corresponds to 0.05 %. Film growth is 750 nm in 30 s, which is 25 nm/s ([0082] and [0083]). The method of D1 is considered to be suitable for coating a continuous film or a series of substrates supplied semi-continuously.

Hence, also claims 4, 5, 9, 13, 14, 16, 19 and 20 lack novelty with respect to D1. Further it is assumed that the plasma density in D1 is below the values given in claim 15, because the process of D1 is quite similar than the one of the present application (see also the examples of the application). Therefore, also claim 15 lacks novelty. However, even if this claim would be novel it would not be considered inventive, because the determination of the plasma density is considered as an optimization of the known process of D1. Claim 10 is not considered inventive, since it is obvious that thicker layers or layers of a different composition can be made by sequential coating. Subject-matter of claims 6, 7 and 21 forms state of the art for CVD apparatuses. The skilled person would therefore consider also to equip the apparatus of D1 with such features.

3.2. Also D2 teaches an atmospheric glow discharge plasma CVD process using a titanium alkoxide for deposition of a TiO_2 layer. The Japanese patent application and its computer-translation, provided by the JPO, reveal further details. The substrate temperature may raise up to 200°C [0026]. The apparatus is suitable for providing a laminar precursor gas flow. Such an apparatus is considered to provide the uniformities given in claim 9. An extraction system is implied. Cooling is apparently provided to avoid overheating of the substrate [0026].

Note also that [0011] and [0030] mention use of He gas, as it is the case in the examples of the present application. [0040] describes a photolytic effect.

Claims 1, 4 - 9, 11, 17, 18, 20, 22 - 24 lack novelty with respect to D2.

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3.3. D3 has a publication date between the priority date and the filing date of the present application. It will not be discussed with respect to novelty and inventive step, because for the time being the priority date of the present application is assumed to be validly claimed. D3 discloses deposition of layers by atmospheric plasma CVD (abstract). The coating apparatus is shown in Fig. 1, including a gas extraction system. In the examples, TiO₂ is deposited on cellulose ester films. Hence, it must be assumed that the substrate temperature lays below 250°C. [0018] states that the electrodes are made of stainless steel and may adjust the temperature by water circulation. The plasma density is 0.03 W/cm². Ti precursors are mentioned in [0132].

3.4. D4 is only available in Japanese. However, EP1342810 is a family document, which claims the same priority dates and which is available in English. According to EP1342810 D4 relates to a method of producing anti-reflexion coatings onto organic films by plasma CVD at atmospheric pressure. Deposition of TiO₂ is described on pages 24 - 25. The apparatus and the coating method are taught on pages 6 - 13. Claims 1, 4 - 9, 11- 20 and 22 - 24 lack novelty over D4. Claims 10 and 21 are only considered as technical variations of D4.

3.5. With respect to the prior art documents D1 - D4 claims 2 and 3 are not derivable. However, post-treatment of ceramic films deposited by CVD is known in the art. D5 and D6 mention a plasma treatment of deposited TiN films to improve its electrical properties. It is common knowledge that the electrical properties are strongly related to the stoichiometry and crystallinity of the TiN films. D7 and D8 teach plasma treatment of Ta₂O₅ and of (Ba,Sr)TiO₃ films, the latter containing already TiO₂, to improve their electrical properties by improvement of the crystallinity. Therefore, subject-matter of claims 2 and 3 appears obvious to the skilled person. For example, if the skilled person is not fully satisfied with the optical and/or electrical properties of the TiO₂ films deposited by a method chosen from D1 - D4, he/she would consider the teaching of these documents, i.e. that plasma post-treatment of related TiN, Ta₂O₅ or (Ba, Sr)TiO₃ films may improve the electrical properties.

3.6. D9 is mentioned, because it teaches pre-treatment of a substrate before deposition of TiO₂ by a plasma CVD process (col. 3, line 5 - 9). Pre-treatment is also mentioned in the description of the present application.

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4. Industrial applicability (Article 33(4) PCT).

Claims 1 - 24 fulfill the requirement of industrial applicability, since subject-matter of present application can be made or used (in a technological sense) in industry (Article 33(4) PCT).

Re Item VI

Certain documents cited

Certain published documents

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
D3 = US2003/0072891	April 17, 2003	April 12, 2002	April 25, 2001

Re Item VII

Certain defects in the international application

The application does not comply with the provisions of Rule 5.1.a.ii PCT, because the most relevant prior art, such as documents D1 - D4 are not cited.

Re Item VIII

Certain observations on the international application

Clarity

1. It is not clear what exactly is meant in line 7 of claim 1.
2. Claims 9, 16 - 18, 20 and 22 - 24 are defined by the result to be achieved instead of by definition of technical features which, in combination with the known combination of technical features, would provide these results. A definition of claimed subject-matter by the result to be achieved is only allowable in exceptional cases (see PCT Gazette, section

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IV, paragraph III-4.7).

3. The expression that "the film has a degree of crystallinity" in claim 23 is relative, because it is unclear, what "degree of crystallinity" means: do nuclei comprising a few atoms but having regular interatomic distances already fall under this expression or are small crystals meant? In addition, depending on the structure determination procedure, such as XRD, TEM, and on the size of the "nuclei or crystallites", some materials will not appear crystalline if examined by one method but appear crystalline when examined by the other method.
4. The expression "good optical quality" in claim 24 is relative, because "good" has a different meaning for different persons.
5. Depending claim 3 refers to "the glow discharge post treatment". However in the preceding claims a glow discharge post treatment is not mentioned.
6. Depending claim 10 refers to "the direction of movement". However in the preceding claims a direction of movement is not mentioned.
7. Depending claim 13 refers to "the metal electrodes". However in the preceding claims metal electrodes are not mentioned.

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Claims

1. Method for depositing titania, or titania-containing as thin films on a substrate, the method comprising the steps of:
 - using an atmospheric pressure glow discharge plasma as a major source of reaction to improve film properties and film growth rates, when the substrate is heated at a temperature below 250°C,
 - introducing a reactive titania CVD precursor which has been pre-vaporised into the introduced gas flow into a gas flowing through a coating region,
 - forming thin film, the said film is photo-active, demonstrated by their ability to destroy organic materials on the surface and/or to modify the surface energy on irradiation with UV or visible light
- 10 2. Method according to claim 1 wherein a post treatment of the coating with an atmospheric glow discharge plasma modifies the film properties and structure.
3. Method according to claim 2 wherein the post treatment modifies the film stoichiometry allowing control of film properties.
- 15 4. Method according to claim 1 wherein a laminar flow is introduced into, and through the coating zone.
- 20 5. Method according to anyone of the claims 1 to 4 wherein an extraction system is employed to control gas flow through the coating zone which supports controlled flow.
- 25 6. Method according to anyone of the preceding claims wherein a thermal control system is designed into the coating zone to maintain the substrate temperature at the desired level, said thermal control system can be achieved by a range of techniques including gas or water or liquid coolant based cooling, or combinations thereof.
7. Method according to claim 6 wherein the thermal control system is designed to cool the coating zone to reduce unwanted side reactions.
- 30 8. Method according to claim 1 wherein the reactive titania CVD precursor which is introduced in the coating zone is an alkoxide of titanium or titanium tetrachloride.

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9. Method according to anyone of the preceding claims wherein films can be deposited with a uniformity of at least +/- 20 % and preferably a uniformity of at least +/- 10 % and more preferably better than +/- 5%.
10. Method according to anyone of the preceding claims wherein it can be used to build up a thicker layer or layers of different composition by arranging sequential coating regions along a direction of movement of the substrate.
11. Method according to anyone of the preceding claims wherein it can be used in combination with different coating method.
12. Method according to claim 1 wherein the glow discharge plasma is generated, between metal electrodes, by a low frequency e.g. AF or RF source where the frequency is below 100KHz and preferably below 30Khz
13. Method according to claim 12 wherein the metal electrodes are selected from a material which reduces heat generation
14. Method according to claims 12 or 13 wherein the electrodes are made of brass.
15. Method according to anyone of the preceding claims wherein the power density of the plasma is below 5 Wcm⁻² and preferably below 1Wcm⁻² and more preferably below 0.5 Wcm⁻².
16. Method according to anyone of preceding claims, wherein the peak growth rate is at least 10 nm per second, and up to several tens of nm per second, over 100nm per second.
17. Method according to anyone of preceding claims, wherein the film can be deposited on preformed and/or thermally toughened substrates
18. Method according to anyone of preceding claim, wherein the film can be deposited on a wide range of temperature sensitive substrates including thermally preformed substrates and plastic substrate materials.
19. Method according to anyone of preceding claims, wherein a level of water and oxygen are controlled carefully to achieve target growth rates and to control unwanted side reactions, the oxygen level being below 5% and more preferably below 1%, the water vapour levels being controlled preferably below 1% and more preferably below 0.1%
20. Method according to claim 19, wherein it is suitable for coating moving substrates – both as continuous film or sheet, or a series of substrates supplied semi-continuously.

21. Method according to anyone of preceding claims, wherein one or more gas flushing zones is used to allow the introduction, and removal, of the substrates whilst maintaining the integrity of the coating region gas composition.

22. Substrate according to claim 21, wherein the film is crystallized

5 23. Substrate according to claim 22, wherein the deposited film has a good optical quality suitable, and having an absorption levels, which is low typically from a few % to less than 1, for use on substrates which are required to be substantially transparent to the human eye and to be looked through.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/40 C23C16/453 C23C16/503

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
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EPO-Internal, WPI Data, PAJ

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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.
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<input checked="" type="checkbox"/> Patent family members are listed in annex.
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* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the International search	Date of mailing of the International search report
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1 March 2004	08/03/2004
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer
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Hintermaier, F

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